UV and IR laser spectroscopy of isolated molecular structural dynamics
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Chapter 1

Introduction

1.1 High-resolution laser spectroscopy

Spectroscopy is one of the most powerful tools of a scientist to investigate the surrounding world. Observing how photons interact with matter provides us with invaluable information about the structure, behaviour and function of matter in all its forms; from gasses to solids, from single elements to large and complex molecular structures. In chemistry, spectroscopic methods have proven themselves to be irreplaceable even more than in other fields of science. Often they are the only tool to probe molecular structure and dynamics of intra- and inter-molecular processes at the highest level of detail. The spectral lines observed with spectroscopy give us direct access to what constitutes the quantum-mechanical fingerprint of a molecule: the structure of energy levels. With the help of theoretical analysis these levels can be directly related to physical and chemical properties of molecules like atomic composition, strength and arrangement of chemical bonds, structure, size, shape and so on. Stable systems as well as dynamic processes can be studied.

Unfortunately, the advantage of spectroscopy, i.e., its power to provide rich and detailed information, is often also its drawback. Except for the most simple molecules, the density of possible quantum states a molecule can occupy leads to very complex spectra. This problem scales up quickly with the size of the molecular system and the temperature at which it is studied. Rotational motion of the molecule gives rise to a set of energy levels with separations that are inversely proportional to the moments of inertia of the molecule. These values vary from a few wavenumbers for diatomic systems to $10^{-3}$ cm$^{-1}$ for simple aromatic compounds [1], and even smaller for larger systems. Vibrational energy levels are much more dispersed than rotational levels, but in large molecules they can also easily lead to a high density of spectral lines. The number of energy levels that can be observed in a single molecule is thus growing fast with its size. At the same time, the large number of low-energy quantum states leads to the situation that molecules can be in different energy levels at room temperature. Energy gaps that are observed during
spectroscopic measurements are in general different for each of those starting states. As a result, the observed spectrum provides too much information to be readily analyzed.

To reduce the complexity of spectra, proper measures must be taken. One of them is to aim for a spectral resolution that is as high as possible in order to distinguish close-lying spectral lines. For the problems at hand in the present thesis this can be achieved by utilizing lasers as a very accurate spectroscopic probe. The power of the lasers lies in their capability of focusing energy in a narrow spectral bandwidth and time period. Thanks to them we can generate powerful bursts of photons of identical properties exactly when and where we need them. Individual transitions can be selectively excited and detected with great efficiency.

1.2 Cold and isolated molecules

Another way to make spectra more “readable” is to simplify them by reducing the number of energy levels that a molecule can access at the start of the experiment. In other words, by measuring on ensembles of molecules that are as identical as possible. This can be achieved by reducing the internal energy of molecules. According to the Boltzmann distribution, such cooling leads to the occupation of less energy levels. Spectral transitions and other molecular properties are much more uniform under such conditions, leading to highly-detailed spectra. Typical examples of the huge effects of cooling on the spectral content are given in refs. [1-3]

Apart from internal energy, another source responsible for spectral heterogeneity is the influence of the environment on the molecule. In solid and liquid states, the properties of a single molecule are thus heavily influenced by interactions with other molecules. If we want to measure its intrinsic properties, we must minimize this influence and study the molecules under isolated conditions. Such studies also offer the most direct link to theoretical methods. Comparison of experimental results with theoretical predictions creates a loop that enables both a better understanding of the system studied and improvement of theoretical methods.
1.2.1 Molecular beam spectroscopy

Supersonic molecular beams are one of the well-established techniques to generate cold and isolated molecules [1, 4-6]. The earliest utilized form of molecular beams are effusive beams [7] in which the orifice size $D$ is smaller than the mean free path $\lambda_0$ of the gas particles in the source reservoir. Under such conditions there are almost no collisions between gas particles during the transition from the source reservoir to the vacuum chamber. The velocity distribution and the associated gas temperature are therefore not changed. Even more important from a spectroscopic point of view is the observation that for polyatomic molecules present in the gas there are no mechanisms that can influence efficiently their population distribution over rovibronic states. In short, the state of the gas is not influenced during expansion into the vacuum.

Much more interesting is the case when $D > \lambda_0$. In 1951 Kantrowitz and Gray [8] proposed that gas flow under such conditions could offer a much higher beam density. It was also suggested that additionally a narrowing of the velocity distribution would take place. Molecules and atoms in the supersonic beam are slow with respect to each other and therefore find themselves in a translationally cold bath. As the collisions take place, this low translational temperature is transmitted to the rovibrational levels in accordance with the energy equipartition rule, and the molecules also become internally cold. Although Kantrowitz and Gray were much more interested in the effect of the increased beam density, it is this “cooling side effect” that is responsible for the huge interest in supersonic molecular beams in the years that followed.

Since the early years of supersonic molecular beams, development of the technique had to face the stringent conditions on pump capacities. Large orifice diameters imply a large gas flow into the vacuum chamber, but also large problems with sustaining pressure at a level that will not lead to disturbance of the molecular beam. One of the solutions has been to improve the performance of vacuum pumps. Another one has been to take advantage of pulsed nozzles. If the orifice is open repeatedly for a short time, the overall gas flow can be significantly reduced while spectroscopic measurements can still be performed using pulsed lasers. One of the first technical solutions capable of generating short molecular beam pulses has been the pulsed valve of Hagena [9] that utilized a solenoid-driven plunger with a minimum opening time of 1.6 ms. In the following years other nozzle designs have been proposed providing shorter opening times and faster repetition rates. Examples include the Gentry-Giese design with the “hairpin” opened by the repulsive force between two bars generated by electrical currents in opposite direction [10] that was capable of producing 10 $\mu$s pulses at 1 Hz or 100 $\mu$s pulses at 10 Hz [11, 12], double-solenoid nozzles [13, 14] with opening times of 10-100 $\mu$s and operating at frequencies up to 35 Hz, adopted car fuel injection valves (~500 $\mu$s at 100 Hz) [15, 16] or, more recently, piezoelectric valves reaching high-kHz repetition
rates with pulses shorter than 10 µs [17-22]. The nozzle setup that has been used in the experiments performed for this thesis is described in detail in Chapter 2.

Another advantage of the molecular beam technique is the possibility to create and study molecular clusters [23, 24] that would be very difficult, if not impossible, to synthesise and studied by other means. Clusters of the target molecule with species like water [23, 25-27], methanol [28, 29], carbon dioxide [30, 31] and many others [32-35] can be easily seeded in a molecular beam. In the initial part of the jet expansion collisions promote the generation of weakly-bonded species that subsequently are frozen out at low temperatures. The number of attached species can be controlled by the experimental conditions, while mass-resolved detection techniques provide selectivity of the measurement. The possibility to generate pre-defined molecular clusters offers unique possibilities to study solvation effects as solvent molecules can be added one at a time to the solute [27, 28]. Mixed clusters that contain more than one type of solvent molecules can be studied as well, an example is presented in Chapter 7.

Since a number of years, the cooling step is not only employed to cool down molecules but also to study conformational isomerisation processes. As a result, detailed studies can be made of the minima and the barriers for interconversion between these minima on the potential energy surface of ground and excited states [36-38].

1.2.2 Liquid helium nanodroplet spectroscopy

In recent years, liquid helium nanodroplet spectroscopy has emerged as an alternative means to perform high-resolution spectroscopy on cold, isolated molecules, and is currently attracting a lot of attention from experimentalists and theoreticians alike [39-43]. Historically, the idea that molecules sealed in inert matrices can exhibit properties similar to those of completely isolated species is probably first mentioned in 1924 in the work of Vegard [44], where he mentioned the condensation process of nitrogen dissolved in a noble gas on a cold surface. It took many years before the first experiments utilizing this idea were performed [45, 46], but then the spectroscopy of cold, inert matrices rapidly became a popular and proven technique to study a large variety of molecular systems. Nevertheless, the technique was not without problems since many species exhibited a stronger attraction to the walls of the containing vessel than to the inert matrix, thus leading to a high concentration of the sample outside the matrix. Also, aggregation of dopants within the matrix was observed. The solution to these problems came with the idea of seeding the sample molecules one by one in small droplets of liquid helium. Originally, the “pick-up” technique was studied by Scoles [47, 48] using argon clusters that were seeded with impurities. The first reports concerning pick-up of impurities by a beam of liquid helium nanodroplets were presented by
Toennies [49] followed by spectroscopic studies of Scoles on SF$_6$ in a liquid helium matrix [50, 51]. Studies that paved the way for further use of helium nanodroplets have been the experiments of the Toennies group in which they determined the temperature of the liquid helium nanodroplet as 0.38 K [52], and subsequent studies where the superfluid character of the droplets consisting of more then 60 helium atoms was demonstrated [53]. All these characteristics make liquid helium nanodroplets an excellent environment for the study of cold, isolated molecular systems. Since the pick-up conditions can be easily adjusted, and the pick-up process repeated many times for different species, the method also provides excellent opportunities to study a wide variety of weakly-bonded multi-component complexes [54-57].

As yet, liquid helium nanodroplet spectroscopy has been focused predominantly on the study of neutral molecules, largely because of the difficulties associated with creating ion-containing helium droplets and the absence of sensitive detection techniques. Although other techniques utilizing cryogenically cooled 22-pole ion traps [58] or argon tagging [35] are available for performing spectroscopy on ions, they inheritably suffer from the lack of sensitivity, offer significantly worse cooling capabilities, and often require multiphoton absorption. The present thesis makes a big step forward in the use of liquid helium nanodroplet spectroscopy as it shows how its application area can be extended to charged molecular systems (Chapter 9) [59].

1.3 Towards large molecules

Although high-resolution spectroscopy methods of isolated molecules has more than proven its merits for small and moderately-sized species, problems arise when one tries to apply the same methods on larger systems. The first obstacle is found in obtaining a high enough vapor pressure of the sample. Heating is a well-established and simple method, but as the size of the molecule increases, so does the required temperature and the risk of thermal dissociation of the sample. The laser desorption technique provides an excellent alternative. Originally developed for mass spectroscopy [60, 61], it rapidly found application in optical molecular beam spectroscopy [62-65]. In this method the sample is deposited on a light absorbing surface, usually graphite, and then desorbed with a short laser pulse. Because the heating time is strongly limited and the whole process occurs under thermal nonequilibrium conditions, dissociation of the sample molecules is avoided. After desorption, the isolated species are introduced into a temporally synchronized supersonic jet and thereby cooled. The desorption technique has proven to be capable of bringing various types of molecules into the vapor phase, and has opened molecular beam spectroscopy to previously inaccessible molecular systems like...
mechanically interlocked molecules [66], clusters of DNA-bases [65] and large peptides with masses up to 1900 a.m.u. [67].

Another obstacle to perform high-resolution spectroscopy on larger systems is the capacity to cool them. As the number of atoms in the molecules rises, so does the number of internal degrees of freedom and the amount of internal energy that must be removed from the molecule in order to obtain its low rovibronic temperature. Although the cooling capabilities of a supersonic jet can be improved by using heavier carrier gases [4, 68, 69], the cooling efficiency of the supersonic molecular beam is in general not sufficient for large systems [70, 71]. As a result, electronic excitation spectra often become broad up to the point that structure can no longer be observed and information is lost. Larger cooling capabilities can be achieved in liquid helium nanodroplets [71], especially when pulsed nozzle techniques are utilized that allow the formation of droplets with a size of $10^6$ helium atoms and more [72-74]. Since evaporation of a single helium atom from a nanodroplet releases approximately 5 cm$^{-1}$ of energy [75], this theoretically allows the removal of internal energy from room temperature molecules that consist of thousands of atoms.

1.4 Outline of this thesis

In this thesis high-resolution, isolated-species spectroscopic techniques have been applied on a number of molecular systems that play an important role in biological applications, on molecules that have emerged as important from a molecular nanotechnological point of view, and on molecules that serve as models for a further understanding of energy and charge transport. One of the common topics of these studies is the development of novel spectroscopic approaches to extend the area of application of high-resolution spectroscopy. Chapter 2 gives a detailed description of the experimental setups and spectroscopic techniques that have been employed to this purpose.

Linear $\pi$-conjugated systems have been studied extensively because of their applications in the field of molecular electronics. Organic photovoltaic cells, organic light emitting diodes, molecular transistors and nanowires have been presented by numerous groups. Branched $\pi$-systems, on the other hand, have attracted considerably less attention despite the unique possibilities they could potentially offer. In Chapter 3 the excited and ground state properties of 1,1'-diphenylethylene (DPE), a prototypical branched $\pi$-conjugated system, are investigated using a combined experimental and theoretical approach.

Chapter 4 reports on a study of components that are currently being used for the construction of artificial molecular machinery. One of the problems in performing high-resolution spectroscopy on these systems is the conformational heterogeneity that impedes conformation-specific spectroscopy. In Chapter 4 an approach based on helium
nanodroplets is demonstrated which allows conformationally resolved spectra to be obtained. Moreover, we show that each particular conformation gives rise to a distinct spectral signature that potentially offers a powerful means to identify its specific structural properties.

Electronic relaxation process responsible for the photoprotection mechanisms of DNA bases are currently the subject of extensive debate. Many studies have consequently applied high-resolution spectroscopy on these bases, in particular on adenine. In Chapter 5 such studies are performed under liquid helium nanodroplet conditions. We show that this approach sheds new light on the energy relaxation pathways of the lower electronically excited states. In this Chapter we furthermore investigate to what extent a molecule can be considered as “isolated” in the helium nanodroplet surroundings.

In Chapters 6 to 8 the chromophore of the Photoactive Yellow Protein, para-coumaric acid, is studied. This molecule has been a constant challenge and headache for spectroscopists as many have tried - unsuccessfully - to characterize its electronically excited states under cold, isolated conditions. Here, the first absorption and excitation spectra of para-coumaric acid are presented that enable us to study in detail its conformational heterogeneity, excited state geometry, and photodynamics. Chapter 7 reports on the thermal dissociation processes of para-coumaric acid, and the spectroscopic properties of the resulting 4-hydroxystyrene-CO₂ cluster. Electronic relaxation processes and the influence of a biological environment are elucidated in Chapter 8 where methyl-4-hydroxycinnamate and its water cluster are studied.

In Chapter 9 we describe the development of a novel technique to perform high-resolution spectroscopy on charged species in liquid helium nanodroplets. Taking the aniline cation as a prototypical example, we explore its sensitivity performance and the physical processes that are at the basis of this sensitivity. Finally, experiments on the aniline dimer cation are performed to assess the potential of the technique to map out charge distributions in extended molecular systems.
References